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Biodegradation of a new polymer binder based on modified starch in a water environment

Biodegradacja nowego spoiwa polimerowego na bazie skrobi modyfikowanej w środowisku wodnym

Abstract
In this study, the results of biodegradability of a new polymeric binder consisting of modified starch – Polvitex Z (by Xenon) in a water solution are presented. Biodegradation tests were conducted in accordance with the Zahn–Wellens method, which is intended to denote the susceptibility to biodegradation by microorganisms (in high concentrations during the static test) of the non-volatile, watersoluble organic compounds.
Observations of the decomposition process were carried out through regular, daily or at certain time intervals by measurement the Chemical Oxygen Demand (COD) and level of biodegradability (RT) in the prepared samples during the test. The study showed that the starch binder is fully biodegradable material in an aqueous medium.

Key words: biopolymers, polymer binders, moulding sands, biodegradation

Streszczenie
W niniejszej pracy zostały omówione wyniki badań stopnia biodegradacji roztworu wodnego modyfikatu skrobiowego Polvitex Z firmy Xenon – materiału polimerowego użytego jako spoiwo do mas formierskich. Testy biodegradacji przeprowadzono zgodnie z metodą Zahna–Wellensa, która ma na celu oznaczenie podatności nielotnych, rozpuszczalnych w wodzie związków organicznych na biodegradacje przez mikroorganizmy występujące w dużym stężeniu podczas badania statycznego. Obserwacje procesu rozkładu prowadzono przez regularne, codzienne lub w określonych przedziałach czasowych pomiary chemicznego zapotrzebowania na tlen (ChZT)

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i stopnia biodegradacji (R_T), mierzonych w przygotowanych próbkach w trakcie trwania testu. Przeprowadzone badania wykazały, że spoiwo skrobiowe jest materiałem w pełni biodegradowalnym w środowisku wodnym.

Słowa kluczowe: biopolimery, spoiwa polimerowe, masy formierskie, biodegradacja

1. Introduction

Natural polymers are a group of materials, which are gaining wide popularity in recent years, such as in medicine and in the packaging field, because of their specific properties. Is a noticeable increase in the production of these materials, so that the availability to them is much easier and the area of their application is expanding [1–4].

In the foundry industry polymers are mainly used as the binder grains of sand or material, which support binding properties of adhesives. Commonly used binders for foundry drawn up on the basis of synthetic resins have good technological properties, however, are harmful to the environment [5]. Therefore, research is conducted aimed to develop a biopolymer binders, which in terms of technology and economics will constitute an interesting alternative bonding in moulding sands technologies [6–12].

Waste generated by foundries during the production of castings are mainly the used sands, whose mass may exceed even several times the mass of produced castings, so that we cannot fail to notice the problem of waste and recycling of moulding materials [13]. Therefore, renewability of used sands and the biodegradability of polymers applied in foundry is a desirable feature due to stricter environmental regulations and the spectrum of the energy crisis [14].

An example of biopolymer used in moulding is starch and its derivatives. Starch belongs to the group of polysaccharides and irrespective of the botanical origin is biopolymer, composed of linked glucose repeating units of α-1,4-glycosidic linkages in amylose, amylopectin and α-1,4- and α-1,6-glycosidic bonds. The chemical composition of the starch is not homogeneous and consists of amylose (20–25%) and amylopectin (75–80%) Amylose forms viscous solutions at 90°C, and amylopectin at 70°C forms a hydrogel. The disadvantage of native starch is its insolubility in cold water and only a temperature of about 70°C begins to swell and partially dissolve [15–17].

Native starch prevents defects of castings associated with the moulds distensibility due to the fact that in the process of heating allows to sand deformation occur without any deformation of the mould [13]. The starch is II or III class binder bond by dehydration (drying temperature of 160–180°C). The technology has been used as a form of so-called cooked starch, is introduced into the core sand mainly to increase the strength of the mass prior to curing or drying [5, 18].

Carboxymethyl starch (CMS) is an example of etherified starch [17]. Depending on the reaction conditions for preparing carboxymethyl starch are obtained substances with different characteristics. Compared to the native starch modified starch exhibits superior binding capacity of the sand grains in the core sands, which is connected with an increase in the degree of the substitution (DS). Changes in the starch molecule are determined by the degree of DS, which is defined as the average number of substituted hydroxyl groups in each glucopyranose ring. Also, viscosity, water solubility and the stability of the CMS are increased in proportion to the degree of the substitution. Suitable parameters of binders for the core sand with the CMS are already achieved with a degree of substitution in the range 0.3–0.5 – the moulding sand has the best resistance to humidity [19–22].

The possibility of modifying the starch leads to used it as a novel binding agents in the foundry. Modified starch binder has a suitable viscosity and high affinity binding as compared with a binder based on a pure starch. Moulding bonded by the modified starch has good technological properties and is characterized by optimum bending strength about 2 MPa [20–22].

The aim of this study is research conducted over the progress of the biodegradation process polymeric binder based on modified starch. Biodegradation is carried out in an aqueous medium. The degree of biodegradation binder was determined.

2. Materials and methods

2.1. Materials

The following samples were subjected to the biodegradation:

- new biopolymeric binder for foundry based on the modified starch potato (Polvitex Z, Xenon) as a 5% aqueous solution. The solution viscosity of about 13 000 – 28 000 mPa·s and a pH = 10,6;
- ethylene glycol (GE) as a standard (reference value of the biodegradation degree > 90%);
- reference sample (0) containing only activated sludge and a nutrient component (blank test).

The activated sludge

In the research were used an activated sludge coming from the Central Laboratory of Urban Water Supply and Sewerage Company (MPWiK SA) in Krakow.

Activated sludge from all reactors was qualified for I class in the Sludge Biotic Index, it means that the precipitate is very well colonized by microorganisms and processes occurring therein are stabilized [23]. Activated sludge in all bioreactors is characterized by dark color and earthy smell.

Depending on the reactor from which the sample was collected in the activated sludge is dominated by:

- crawling ciliates,
- amoebas,
- sedentary ciliates.

2.2. Methods of testing

Biodegradation tests bio-polymer binders in aqueous environment

Biodegradation tests were performed by the Zahn–Wellens test [24]. This method is intended to denote the susceptibility to biodegradation of the non-volatile, water soluble organic compounds by microorganisms present in high concentrations during the static test.

This method is used for the study of organic substances, which:

- are soluble in water under experimental conditions,
- have a low vapor pressure at the experimental conditions,
- do not inhibit the growth of bacteria,
- are adsorbed in the test system only to a limited extent,
- are not lost by the foaming from the test solution.

Biodegradation test in this method is carried out in vessels (capacity of 1–4 dm^3), which are equipped with devices for mixing and aerating. In these vessels are placed in the activated sludge, nutrients and substances in the test solution as the sole source of carbon dioxide (concentration range 50–400 mg/dm^3).

Measurements of the chemical oxygen demand

In the three glass beakers with a capacity of 250 cm^3 sludge, bacteria solution biopolymer and a binder solution (an aqueous modified starch), ethylene glycol – GE as a standard, activated sludge as blanks – 0 was provided. The test solution is subject to continuous agitation and aeration at 20–25°C in diffuse light or in the dark for 28 days. Temperature, pH and measured the degree of oxygenation were controlled every day.

Observations of the decomposition process were carried out through regular, daily or at certain time intervals measurements Chemical Oxygen Demand (COD). At the beginning of the experiment, the ratio of the COD value (lower after each interval), to the value determined every 3 hours was determined. This ratio is used to determine the R_T factors of bio-decomposition over time and may be determined from the relationship:

$$R_T(\%) = [1 - \frac{(C_T - C_B)}{(C_A - C_{BA})}] * 100 \qquad (1)$$

where:

R_T – biodegradation (%) at time T,

C_A – COD values in the test mixture measured three hours after the beginning of the test (mg/l),

C_T – COD values in the test mixture at time of sampling (mg/l),

C_B – COD value of the blank at time of sampling (mg/l),

C_{BA} – COD value of the blank, measured three hours after the beginning of the test (mg/l).

a) b)

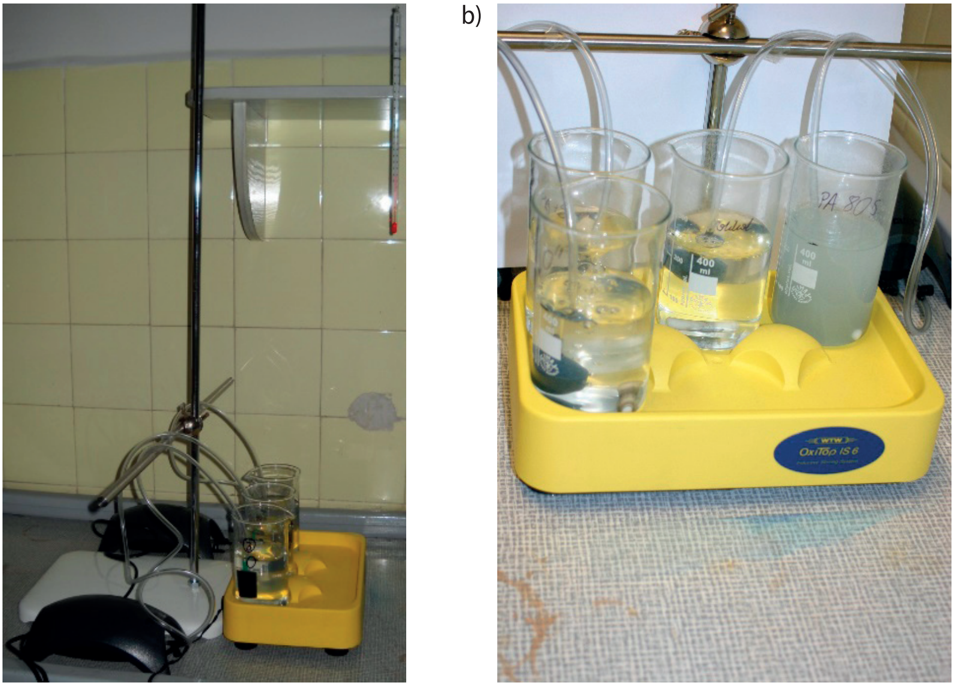

Fig. 1. The test stand (a) to studies of samples (b) biodegradability in the environment

The extent of degradation is rounded to the nearest full percent [24].

Figure 1 shows the test stand to study of samples biodegradation the in the water environment.

3. Results and discussion

During the test the temperature, pH, and turbidity of the aeration level of the individual samples were regularly controlled. According to the requirements of the standard for the whole duration of the test, the pH was maintained at 7–8.

The decomposition process was monitored at regular intervals by measuring the COD. These studies were carried out in the Central Laboratory MPWiK SA using dichromates spectral methods for the determination of the COD.

In accordance with the test requirements the COD value was estimated in selected time intervals. The COD results (decreasing after each interval) compared to the value determined after 3 hours from the moment of the test beginning provides the percentage biodegradation value.

Table 1 shows results of measurements COD for GE and starch-based binder samples.

Table 1. Results of COD measurements

Time, [h]		3	24	48	120	168	288	360	456	512	624	672
day		–	1	2	5	7	12	15	19	21	26	28
0	**COD, mg/lO2**	20,7	20,4	25,8	31,5	51,8	158	176	165	157	160	162
GE	**COD, mg/lO2**	1251	1160	1110	997	985	743	588	236	212	215	214
Polvitex Z	**COD, mg/lO2**	980	910	801	570	440	460	445	405	380	311	302

On the basis of the COD value of the degree of degradation R_T was determined using the formula (1).

Table 2 shows results of calculations R_T for GE and starch-based binder samples.

Table 2. The R_T[%] results for testing samples

Time, [h]		24	48	120	168	288	360	456	512	624	672
day		1	2	5	7	12	15	19	21	26	28
GE	**RT, [%]**	7,37	11,88	21,52	24,15	52,45	66,51	94,23	95,53	95,53	95,77
Polvitex Z	**RT, [%]**	7,27	19,19	43,87	59,53	68,52	71,96	74,98	76,75	84,26	85,41

The calculated R_T values are presented in the graph as a function of the biodegradation time, providing the biodegradation curve (Fig. 2).

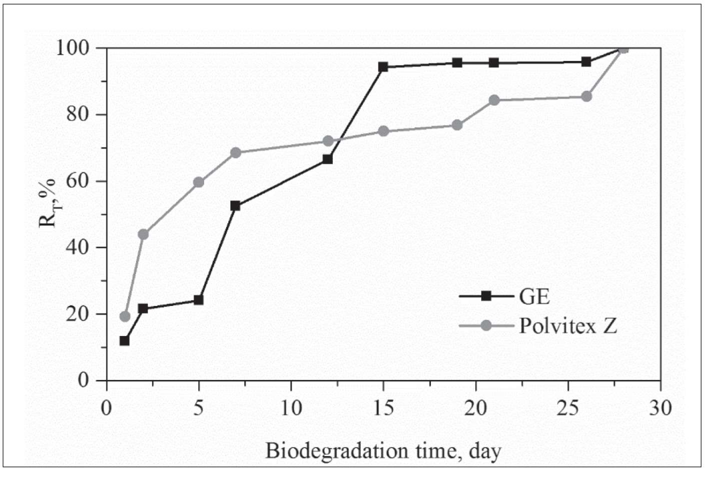

Fig. 2. The biodegradation curves of glycol ethylene (GE) and starch binder (Polvitex Z)

A polymer is considered to be biodegradable when its biodegradation degree after 28 days of a cycle reaches at least 60% [24]. This condition was satisfied by the binder sample.

Analyzing the biodegradation curves shown in Figure noticeable is the rapid and complete decomposition of the reference mixture – GE. However, in the early stages of testing, the starch-based binder was exhibited a greater degree of decomposition. The binder sample to 12 day of test underwent bio-decomposition faster compared to the standard. The R_T value after 12 days for GE was 52.45%, and for starch binder 68.52%. Further progress of binder bio-decomposition of starch was not as intense.

The degree of decomposition of the starch-based binder after 28 days was 85.41%, it means that the test polymer can be considered to group of biodegradable substances. After 28 days the GE sample has nearly in 100% biodegradable.

4. Summary

In this study were carried out the studies on degradation of the binder in the form of 5% aqueous solution of the sodium salt of a modified starch. These measurements were performed in an aqueous environment using a static Zahn–Wellens test.

The paper presents the course of the cycle of the biodegradation. The degradation process was monitored for 28 days, it was important to maintain the test samples suitable conditions such as temperature, pH, oxygenation level and limiting access of light. Maintaining the temperature, pH and degree of oxygenation within the required limits has ensured the correct course of the biodegradation reaction under the influence of microorganisms.

The study demonstrated a high decomposition ratio of biopolymer binder, in the last day of the test the R_T index reached the value of 85%, therefore, on the basis of the standards, the substance can be considered as fully biodegradable.

In this case the result of the study on biodegradation in the aquatic environment gives us information about possibility of modified starch solution as Polvitex Z decomposition in water, and the expected progress this process.

Based on the survey, analysis the results and observations conducted during the test, can be drawn the following conclusions:

- to ensure the proper conduct of the decomposition process very important is proper preparation of the test bench,
- change of temperature, lack of oxygen or exposure of the sample to light can delay or completely stop the process of biodegradation,
- on the 12th day of the test, the degree of degradation of the test composition was 68%, therefore the discussed biopolymer binder is completely biodegradable,
- after 28 days of the test, a degree of decomposition of modified starch was about 85%. Therefore, the tested component of polymeric foundry binder can be classified as environment friendly.

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